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Metal–polymer composite with nanostructured filler particles and amplified physical properties

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The limits of conductivity of a novel elastomeric matrix–nanostructured nickel powder composite are reported. The conductivity falls by a factor of $\geqslant 2 \times 10^{14}$ for compression and by a similar amount in extension. Uncompressed and highly compressed composite displays ohmic behavior but between these limits the current-voltage characteristics are highly nonlinear. The matrix intimately coats the filler so that even above the expected percolation threshold the composite has a very low conductivity. The conductivity of the composite is increased under all mechanical deformations. These and other unusual properties are amplified versions of smaller effects seen in composites containing less highly structured fillers. © *2006 American Institute of Physics*.
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Electrically conductive composites fabricated from insulating polymer matrices and conductive filler particles are used for many commercial applications.[1,2] The properties of these composites have been studied since the 1950s and continue to be the focus of theoretical and experimental studies.[3–5] The conductivity of these composites can be described, once particle shape or agglomeration is taken into account, by statistical percolation[2] or an effective medium model.[3] The conductivity rises rapidly from a value close to that of the matrix when the filler fraction exceeds the percolation threshold. This ranges from $\leqslant 1\%$ to $>10\%$ by volume with the lowest values for fine fibers, e.g. carbon nanotubes, and the highest for spherical particles.

The conductivity of such composites usually increases in compression, as the separation of the filler particles decreases, and falls when the composite is stretched. Wide variations in response are reported for different composites. Typically in compression the conductivity rises by a factor of a few hundred[6] although in uniaxially oriented composites close to the percolation threshold the range is much larger.[7] Exceptionally a decrease in conductivity is seen for a carbon black–silicone composite loaded above the percolation regime.[8] In extension the decreases in conductivity are in the range $10-10^4$ times. An irreversible increase has been observed in composites deformed beyond their elastic limit.[9] Many conductive composites display a positive temperature coefficient of resistance[1,2] so that at high currents the conductivity falls due to expansion and changes in morphology caused by Joule heating. However, at constant temperature composites usually display ohmic behavior. Nonlinear current-voltage characteristics have been reported for anisotropic epoxy resin–graphite flake composites[10] and were attributed to the contacts between the filler particles acting as nonlinear resistors. Thus, although specific composites can display properties that deviate from the norm no single composite displays a combination of such unusual properties.

The present work shows that a new composite, QTC™, produced by a patented process,[11] has extremely large, reversible increases in conductivity when compressed, stretched, bent, or twisted. The response to an applied voltage varies from ohmic to nonlinear and hysteretic depending on the degree of deformation. QTC™ has an elatomeric matrix, e.g. Alphasil 200 (Alphas Industries), Silcoset 153 (Ambersil), Silastic T4 (Dow Corning), F42 (Techsil), containing Inco nickel powder, e.g., types 123 or 287. The particles in these powders have surfaces covered in sharp protrusions. The powders are used as supplied, mixed carefully with the liquid monomers, and the mixture is calendered and cured according to the manufacturer's instructions to produce sheets 1–2 mm thick. The sheets are flexible and recover elastically from ~80% compression and ~40% elongation. Filler to monomer loading is normally in the range 4:1–6:1 by weight, equivalent to volume fractions above the percolation threshold typical of other composites. However, the as made composite is insulating.

The morphology of QTC™ is seen in electron micrographs of freeze fracture and cut surfaces reported earlier.[12] These show that all the metal particles are coated in polymer, which adheres intimately to the nickel, and that the spiky surface morphology of the filler particles is retained in the composite. New scanning electron microscope (SEM) images of cut surfaces of stretched samples [Figs. 1(a) and 1(b)] confirm these findings and show the high density of filler particles. The retention of the filler particle morphology is crucial in determining the properties of QTC™.

The composite is very sensitive to deformation and the conductivity of undeformed QTC™ was determined for a sheet cast directly between aluminum foil contacts using a Keithley 610C electrometer. The conductivity was found to be $1.41 \pm 0.14 \times 10^{-11}$ S m^{-1}. The undeformed composite shows ohmic behavior (Fig. 2). Sample resistance falls with compression, initially exponentially, but at high compression decreases more slowly and eventually falls below the residual circuit resistance. Contact resistance for a variety of metals, e.g., Au, Al, Fe, Cu, etc., is found to be small. Allowing for these factors and large changes in sample size and

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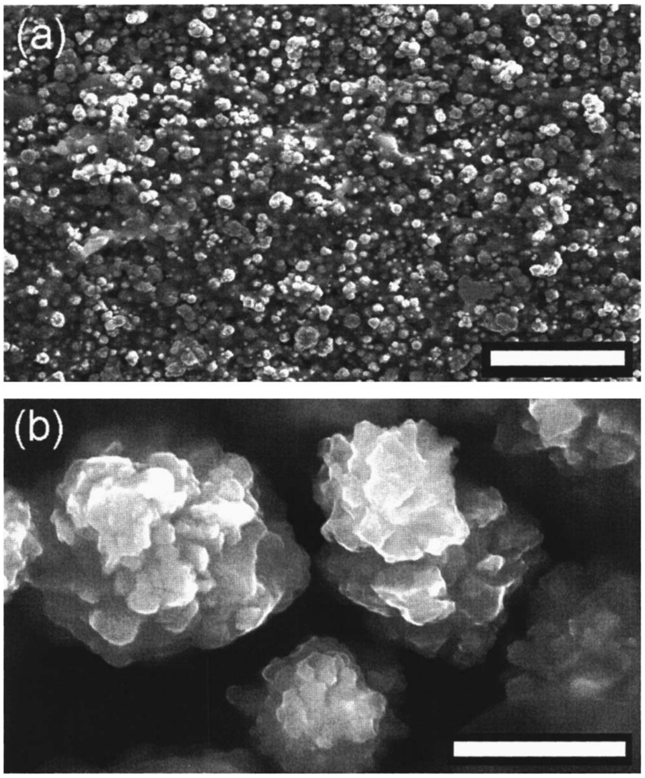

FIG. 1. SEM images of the cut surface of a sample of QTC™ (elongated by 32% ±2%). White scale bars denote: (a) 50 μm and (b) 2 μm.

shape the upper limit of conductivity is estimated to be $\geqslant 3 \pm 2 \times 10^3$ S m^{-1}. The $\geqslant 2 \times 10^{14}$ variation in conductivity exceeds that seen in anisotropic composites[7] by a factor 10^3. The highly compressed composite also has an ohmic response, with a very small deviation due to Joule heating, and can carry currents of several amperes without any sign of damage (Fig. 3).

There is a similar increase in conductivity when QTC™ sheets are stretched. The sample shown in Fig. 1, initially measuring $2 \times 2 \times 10$ mm, was stretched by 32% ±2% in the direction of the longest edge when the resistance, measured in the same direction, was 30 Ω. As reported previously the resistance of a $1 \times 20 \times 20$ mm sheet, measured in the direction of elongation, fell from $\sim 10^{12}$ to 20 Ω at 36% elongation.[12] Ryvkina *et al.*[8] note that in a heavily loaded, uniaxially compressed composite the random network of percolation paths will contain more lateral contacts than axial contacts between filler particles. Lateral expansion accompanying compression accounts for the small, unexpected decrease in conductivity they observed. In stretched QTC™ the large lateral contraction will reduce lateral particle separation and increase conductivity. There is evidence that the effect is amplified because charge transport occurs by field-assisted (Fowler–Nordheim) tunneling. The projections on the surfaces of the filler particles have tip radii below 10 nm.[12] The local field at the these tips will be much larger than that at the surface of a spherical particle.[13] Localized discharge to air when 240 V ac is applied to compressed cylindrical QTC™ samples, i.e., there are internal fields $>3 \times 10^6$ V m^{-1}, supports this hypothesis. Further evidence for this is that removal of the sharp features from the filler particles, by mechanical working, oxidation, or etching, drastically reduces the sensitivity of QTC™ to deformation.[12] Although the uncoated filler particles can be damaged the composite is remarkably robust. Properties are recovered after $>80\%$ compression. It appears that the susceptibility to damage of the Ni particles is significantly reduced by the penetration of the matrix polymer into the voids between the features on the surface of the particles.

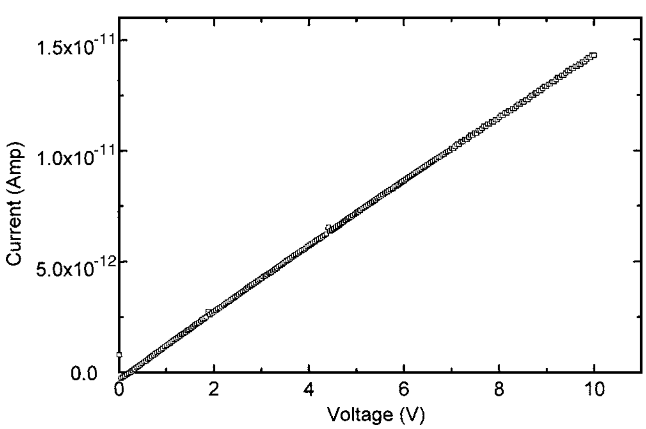

FIG. 2. Current-voltage characteristic of an undeformed sample of QTC™. Data are shown for increasing and decreasing voltage.

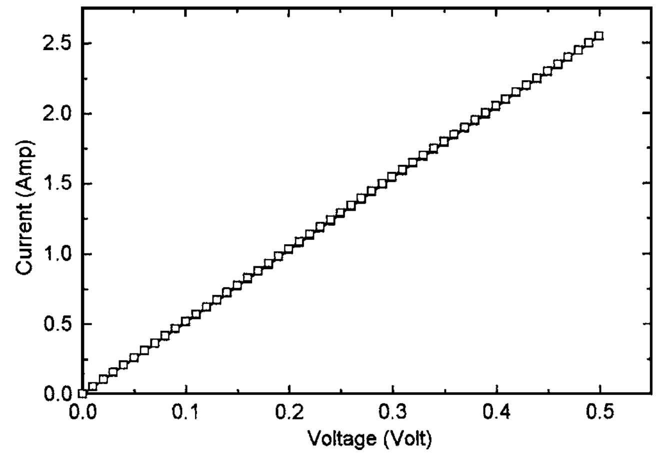

FIG. 3. Current-voltage characteristic of a sample of QTC™ uniaxially compressed to a resistance of ~ 0.17 Ω (70% ±0.5% compression, residual circuit resistance 0.02 Ω). Data are shown for increasing and decreasing voltage.

In other than the low and high conductivity limits (zero and high compression) the electrical behavior of QTC™ is nonlinear and depends on the electrical and mechanical history of the sample. The nonlinear behavior of a 3.5 mm diam, 2 mm thick sample of QTC™ compressed to an initial resistance of ~ 26 kΩ is shown in Fig. 4. As the voltage is increased the current increases nonlinearly to reach a maximum value at about 18 V. It then falls to a low value at the highest voltage. As the voltage is decreased the current increases slowly until there is a rapid rise at ~ 10 V. On reducing the voltage to zero the final resistance, ~ 70 Ω, is lower than the initial value. The characteristic is visibly noisy for increasing voltage above 15 V. These effects are not due to Joule heating as the increase in sample temperature is small, but can be understood in terms of charge trapping on the filler particles. Below 18 V the behavior is similar to that of a varistor, i.e., consistent with Fowler–Nordheim tunneling.[14] A model, in which charge stored at "dead ends" in the percolation network creates potential barriers in adjoining active paths eventually pinching them off, has been proposed.[12] Re-

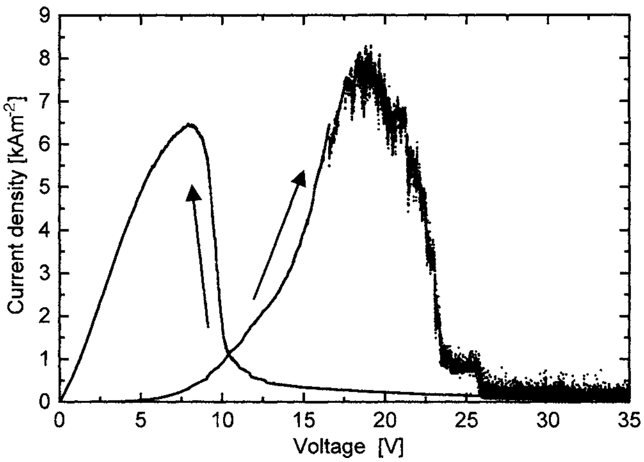

FIG. 4. Current-voltage characteristic of a sample of QTC™ uniaxially compressed to give an initial resistance of 26 kΩ ($17\% \pm 1\%$ compression).

distribution of the trapped charge causes the jumps in current seen in Fig. 4; decaying oscillations with frequencies between 10 and 30 MHz have also been observed. The coherent oscillations associated with an intrinsic negative resistance are not observed. Some of the stored charge leaks away when the applied voltage is reduced. However, some remains and, as the matrix is deformable, alters the configuration of the randomly distributed particles giving a lower final resistance. Compressing the sample to the highly conducting state discharges the sample and the initial behavior is recovered. Otherwise the charge leaks away slowly and the electrical response is altered depending on the residual stored charge. These effects will be described in detail elsewhere.

The enhanced physical properties of QTC™ are a consequence of the nanoscale structure of the filler particles, which are intimately coated by the matrix polymer. The changes in resistance produced by external factors have ranges larger than those of either other isotropic composites or field-structured anisotropic composites.[7] Ohmic behavior is seen in undeformed and highly compressed QTC™ since charge trapping is negligible as either the current is very small or the conductivity is high. Between these extremes the electrical response is highly nonlinear as a consequence of charge trapping on the filler particles and field assisted tunneling. Applications of QTC™ include switches, controllers, tactile sensors,[15] and vapor sensing.[16]

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